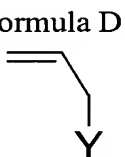
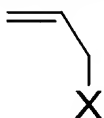
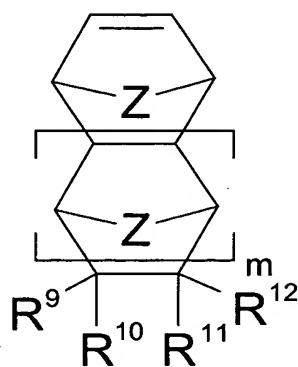
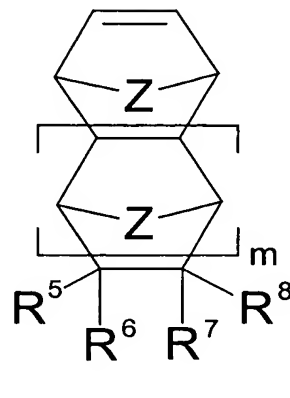
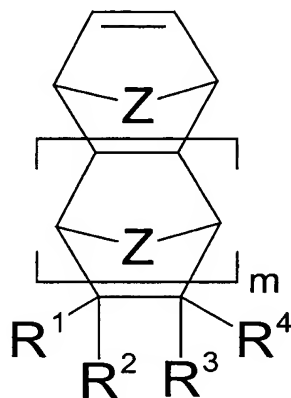


We Claim:

1. A dissolution rate modifier, comprising:  
an oligomer comprising repeating units derived from monomers in accordance with one or more of Formulae A, B, C, D or E:



said repeating units comprising a first repeating unit derived monomers comprising a fluorinated acid labile group substituent according to Formula A and/or Formula E, and optionally other

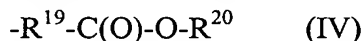
repeating units comprising one or more of the monomers according to Formulae A, B, C, D or E, with the proviso that if a monomer according to Formula A is not present, a monomer according to Formula E must be included and if a monomer according to Formulae D or E are present at least one monomer according to Formulae A, B or C must be present, with the proviso that where at least one repeating unit is derived from Formulae D or E, deriving the oligomer comprises employing a free radical catalyst and where said repeating units are only derived from monomers according to Formulae A, B and/or C, deriving the oligomer comprises employing a Ni or Pd comprising catalyst;

wherein m is an integer from 0 to 5; Z is  $-\text{CH}_2-$ ,  $-\text{CH}_2\text{-CH}_2-$ ,  $-\text{O}-$ ,  $-\text{S}-$ , or  $-\text{NH}-$ ; wherein at least one substituent  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$ , independently, is a fluorinated carbinol having from 1 to about 10 carbon atoms optionally protected by an acid labile group, and the remaining  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and  $\text{R}^4$ , independently, are hydrogen, halogen, or a hydrocarbyl containing from 1 to about 20 carbon atoms, or a hydrocarbyl having from 1 to about 20 carbon atoms substituted at any hydrogen atom with an O, S, N, or Si, or a fluorinated hydrocarbyl having from 1 to about 20 carbon atoms wherein each carbon atom, independently, is substituted with 0, 1, 2, or 3 fluorine atoms; wherein at least one of  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ , or  $\text{R}^8$  independently contain an acid labile moiety, and the remaining one or more  $\text{R}^5$ ,  $\text{R}^6$ ,  $\text{R}^7$ , or  $\text{R}^8$ , independently are hydrogen, halogen, or a hydrocarbyl having from 1 to about 20 carbon atoms, or a hydrocarbyl having from 1 to about 20 carbon atoms substituted at any hydrogen atom with an O, S, N, or Si, or a fluorinated hydrocarbyl having from 1 to about 20 carbon atoms wherein each carbon atom, independently, is substituted with 0, 1, 2, or 3 fluorine atoms; wherein  $\text{R}^9$ ,  $\text{R}^{10}$ ,  $\text{R}^{11}$ , or  $\text{R}^{12}$  are independently selected from a hydrogen atom, a hydrocarbyl having from 1 to about 20 carbon atoms, and a hydrocarbyl having from 1 to about 20 carbon atoms substituted at any hydrogen atom, with O, S, N, or Si, and optionally contain an epoxy, hydroxyl, and/or carboxylic acid functional group; wherein Y is a fluorinated carbinol having from 1 to about 10 carbon atoms optionally protected by an acid labile group, X is OH, CN,  $\text{OC}(\text{O})\text{R}^{13}$ ,  $\text{C}(\text{O})\text{OR}^{13}$ ,  $\text{OR}^{13}$ ,  $\text{N}(\text{R}^{13})_2$ , where  $\text{R}^{13}$  is a linear or branched or cyclic aliphatic hydrocarbyl group containing 1 to about 12 carbons atoms and optionally at least one carbon atom of said hydrocarbyl contains 1, 2, or 3 fluorine atoms; and said oligomer having a weight average molecular weight (Mw) of less than about 3,000 as measured by Gel Permeation Chromatography.

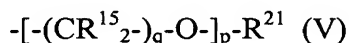
2. The dissolution rate modifier according to claim 1, wherein at least one occurrence of Y, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, or R<sup>4</sup> is a fluorinated group according to the formula -((CH<sub>2</sub>)<sub>n</sub>O)<sub>n'</sub>-CH<sub>2</sub>-C(OR')(CF<sub>3</sub>)<sub>2</sub> wherein R' is H or an acid labile group, and n and n' are independently from 0 to 10.

3. The dissolution rate modifier according to claim 2, wherein the acid labile group is selected from the group consisting of -CH<sub>2</sub>OCH<sub>3</sub>, -CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>, -C(CH<sub>3</sub>)<sub>3</sub>, -Si(CH<sub>3</sub>)<sub>3</sub>, -CH<sub>2</sub>COO(t-Bu), 2-methylnorbornyl, 2-methylisobornyl, 2-methyl-2-adamantyl, tetrahydrofuranyl, tetrahydropyranoyl, 3-oxocyclohexanonyl, mevalonic lactonyl, dicyclopropylmethyl, dimethylcyclopropylmethyl, and combinations thereof.

4. The dissolution rate modifier according to claim 1, wherein at least one of R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, and R<sup>8</sup> comprises a group according to Formula (IV):

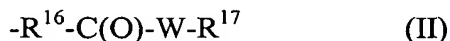


wherein R<sup>19</sup> is selected from C<sub>1</sub> to C<sub>12</sub> linear, branched, or cyclic alkylene, and R<sup>20</sup> is selected from C<sub>1</sub> to C<sub>22</sub> linear, branched, or cyclic alkyl, aralkyl, or alkaryl, and a hydroxy alkyl ether according to Formula (V):



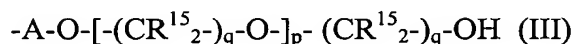
where each occurrence of R<sup>15</sup> is independently selected from H, methyl, ethyl and a halide, q is from 1 to 5, p is from 1 to 20, and R<sup>21</sup> is selected from C<sub>1</sub> to C<sub>22</sub> linear, branched, or cyclic alkyl, aralkyl, or alkaryl.

5. The dissolution rate modifier according to claim 1, wherein at least one occurrence of R<sup>9</sup>, R<sup>10</sup>, R<sup>11</sup>, and R<sup>12</sup> is independently selected from a group according to Formula (II):



wherein R<sup>16</sup> is selected from a covalent bond, C<sub>1</sub> to C<sub>25</sub> linear, branched, or cyclic alkylene, arylene, aralkylene, alkarylene, alkenylene or alkynylene, which can optionally contain halides; W is selected from O, S, and NR<sup>18</sup>, wherein R<sup>18</sup> is selected from H, and C<sub>1</sub> to C<sub>6</sub> linear, branched, or cyclic alkyl; and R<sup>17</sup> is selected from H, C<sub>1</sub> to C<sub>25</sub> linear, branched, or cyclic alkyl, aryl, aralkyl, alkaryl, alkenyl or alkynyl, which can optionally contain halides, and -OH, alkyl,

aralkyl, and alkaryl terminated poly(alkyleneoxide) radicals; and a hydroxy alkyl ether according to Formula (III):



wherein A is a linking group selected from C<sub>1</sub> to C<sub>6</sub> linear, branched, or cyclic alkylene, each occurrence of R<sup>15</sup> is independently selected from H, methyl, ethyl and a halide, q is from 1 to 5, and p is from 0 to 3;

6. The dissolution rate modifier according to claim 1, wherein the acid labile group is a group according to the formula



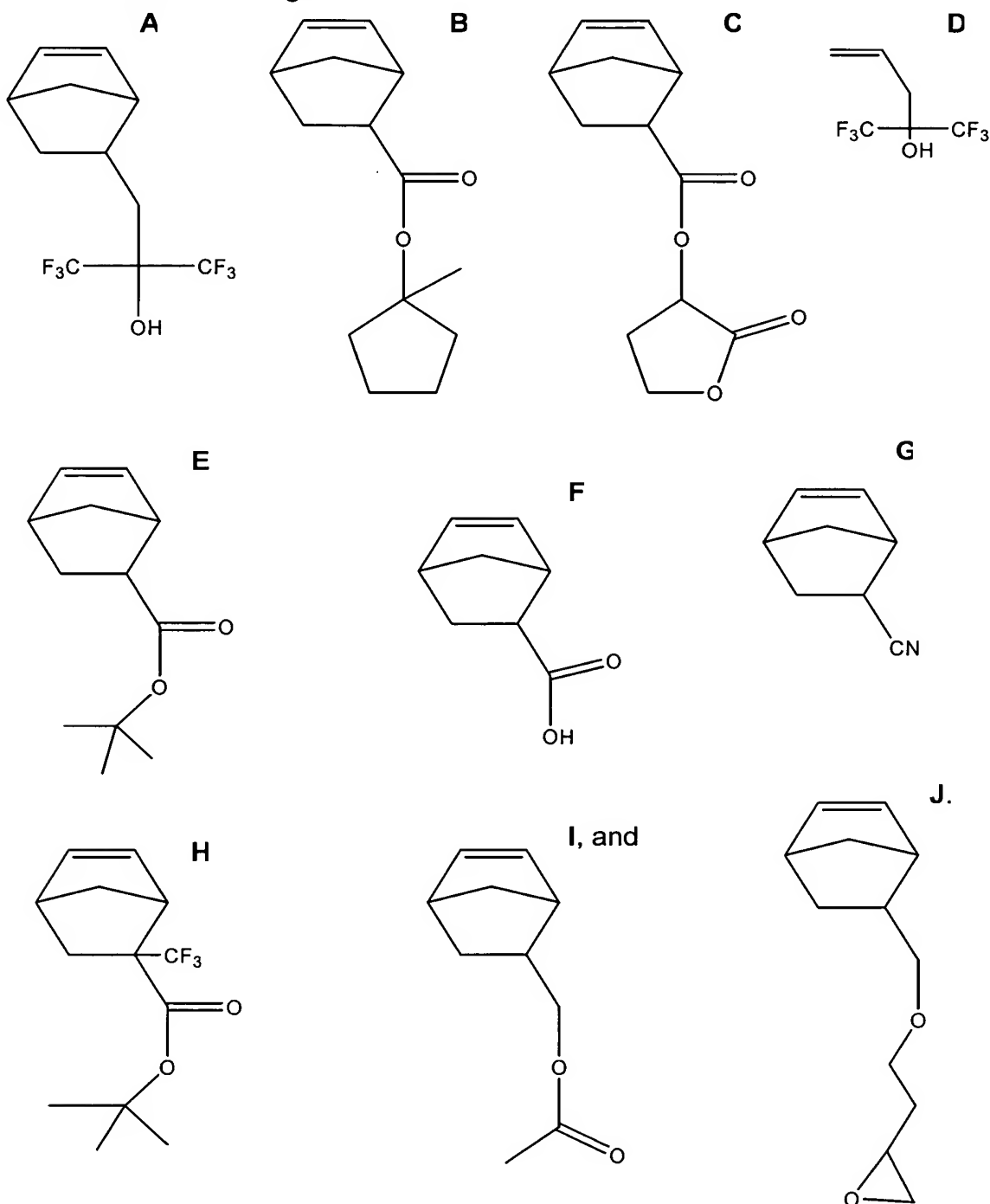
where R'' is selected from -C(CH<sub>3</sub>)<sub>3</sub>, -Si(CH<sub>3</sub>)<sub>3</sub>, 2-methylnorbornyl, 2-methylisobornyl, 2-methyl-2-adamantyl, tetrahydrofuranyl, tetrahydropyranoyl, 3-oxocyclohexanonyl, mevalonic lactonyl, dicyclopropylmethyl, dimethylcyclopropylmethyl, and combinations thereof.

7. The dissolution rate modifier according to claim 1, wherein the monomer according to Formula D is selected from allyl alcohol, allyl nitrile, and allyl cyanide.

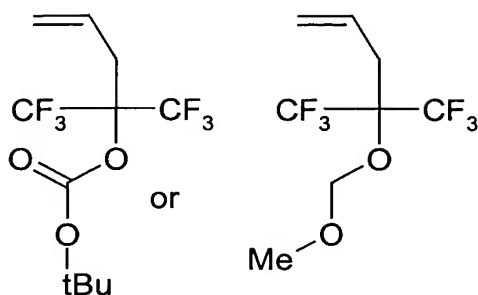
8. The dissolution rate modifier according to claim 1, wherein Y is selected from the group consisting of -(CH<sub>2</sub>)<sub>n</sub>-C(OR')(CF<sub>3</sub>)<sub>2</sub>, in which n is an integer from 0 to 10, and R' is selected from -CH<sub>2</sub>OCH<sub>3</sub>, -CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>, -C(CH<sub>3</sub>)<sub>3</sub>, -Si(CH<sub>3</sub>)<sub>3</sub>, 2-methylnorbornyl, 2-methylisobornyl, 2-methyl-2-adamantyl, tetrahydrofuranyl, tetrahydropyranoyl, 3-oxocyclohexanonyl, mevalonic lactonyl, dicyclopropylmethyl, and dimethylcyclopropylmethyl groups; -C(O)OR'' where R'' is selected from -C(CH<sub>3</sub>)<sub>3</sub>, -Si(CH<sub>3</sub>)<sub>3</sub>, 2-methylnorbornyl, 2-methylisobornyl, 2-methyl-2-adamantyl, tetrahydrofuranyl, tetrahydropyranoyl, 3-oxocyclohexanonyl, mevalonic lactonyl, dicyclopropylmethyl, and dimethylcyclopropylmethyl groups; and combinations thereof.

9. The dissolution rate modifier according to claim 8, wherein Y is -CH<sub>2</sub>OCH<sub>3</sub>, -CH<sub>2</sub>OCH<sub>2</sub>CH<sub>3</sub>, or -C(O)OC(CH<sub>3</sub>)<sub>3</sub>.

10. The dissolution rate modifier according to claim 1, comprising one or monomers selected from structures A through J:



11. The dissolution rate modifier according to claim 1, wherein the monomers according to Formula E comprise:



12. A method of making the oligomers according to claim 1, comprising:
- I) forming a monomer mixture comprising one or more of the monomers according to Formulae A, B, C, D and/or E, wherein if A is not present, E must be included;
  - II) adding a free radical initiator to the monomer mixture in an amount sufficient to effect polymerization; and
  - III) heating the mixture in II) to a temperature at which the initiator can effect polymerization.
13. The method according to claim 12, wherein the initiator is present at a level of from about 1% to 20% by weight of the total weight of the monomer mixture.
14. The method according to claim 12, wherein the free radical initiator is selected from the group consisting of hydrogen peroxide, benzoyl peroxide, di-tert-butyl peroxide, tert-butyl hydroperoxide, azo-bis(isobutyronitrile) and mixtures thereof.
15. The method according to claim 12, carried out in a solvent selected from the group consisting of aliphatics, cycloaliphatics, aromatics, heterocyclics, halogenated aliphatics, halogenated aromatics, ethers and combinations thereof.
16. A method of making the oligomers according to claim 1, comprising:
- i) forming a monomer mixture consisting essentially of one or more monomers according to at least one monomer of Formulae A, B, and/or C and an ethylenically unsaturated material; and

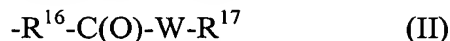
ii) adding a catalyst containing a Ni or Pd complex, wherein the Ni complex comprises a hemilabile, chelating ligand containing a Group 15 and a Group 16 element capable of coordinating to the Ni complex, to the monomer mixture.

17. The method according to claim 16, wherein the monomers according to Formulae A, B, and C comprise monomers wherein groups  $R^1$  through  $R^{15}$  are selected from the group consisting of:

(a) H,  $C_1$  to  $C_{25}$  linear, branched, or cyclic alkyl, aryl, aralkyl, alkaryl, alkenyl and alkynyl;

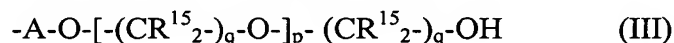
(b)  $C_1$  to  $C_{25}$  linear, branched, or cyclic alkyl, aryl, aralkyl, alkaryl, alkenyl and alkynyl containing one or more hetero atoms selected from O, N, and Si and/or containing one or more halides;

(c) a group according to Formula (II):



wherein  $R^{16}$  is selected from a covalent bond,  $C_1$  to  $C_{25}$  linear, branched, or cyclic alkylene, arylene, aralkylene, alkylene, alkenylene and alkynylene, which can optionally contain halides; W is selected from O, S, and  $NR^{18}$ , wherein  $R^{18}$  is selected from H, and  $C_1$  to  $C_6$  linear, branched, or cyclic alkyl; and  $R^{17}$  is selected from H,  $C_1$  to  $C_{25}$  linear, branched, or cyclic alkyl, aryl, aralkyl, alkaryl, alkenyl and alkynyl, which can optionally contain halides, and  $-OH$ , alkyl, aralkyl, and alkaryl terminated poly(alkyleneoxide) radicals; and

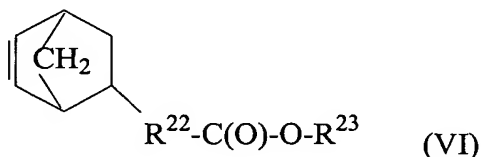
(d) a hydroxy alkyl ether according to Formula (III):



wherein A is a linking group selected from  $C_1$  to  $C_6$  linear, branched, or cyclic alkylene, each occurrence of  $R^{15}$  is independently selected from H, methyl, ethyl and a halide, q is from 1 to 5, and p is from 0 to 3.

18. The method according to claim 16, wherein the ethylenically unsaturated material is selected from the group consisting of ethylene, propylene, butylene, isobutylene, pentene, hexene, and combinations thereof.

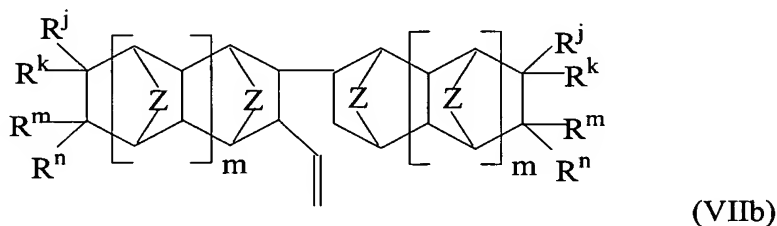
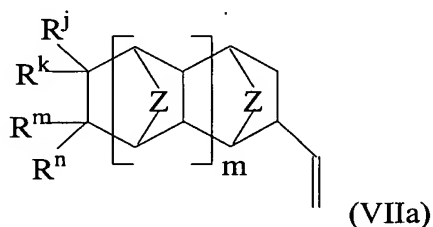
19. The method according to claim 16, wherein the monomers of Formulae A, B, and C include polycyclic olefin monomers according to structure (VI):



wherein  $R^{22}$  is selected from  $C_1$  to  $C_8$  linear and branched alkylene, and  $R^{23}$  is selected from  $C_1$  to  $C_8$  linear and branched alkyl.

20. Oligomers of polycyclic olefin monomers obtained from the method of claim 16.

21. An oligomer according to claim 20, comprising the reaction product of two polycyclic olefin monomers and ethylene including compounds according to Formulae (VIIa) and (VIIb):



wherein each occurrence of Z is independently selected from  $-CH_2-$ ,  $-CH_2-CH_2-$ , O, S, and  $-NH-$ ; each occurrence of m is independently an integer from 0 to 5; and each occurrence of  $R^j$  is described by any of  $R^1$ ,  $R^5$  or  $R^9$ ;  $R^k$  is described by any of  $R^2$ ,  $R^6$ , or  $R^{10}$ ;  $R^m$  is described by any of  $R^3$ ,  $R^7$  or  $R^{11}$ ; and  $R^n$  is described by any of  $R^4$ ,  $R^8$  or  $R^{12}$ .

22. A photoresist composition comprising the dissolution rate modifier according to claim 1.



23. A negative tone photoresist composition comprising:

- A) a solvent;
- B) a photosensitive acid generator;
- C) a crosslinking agent containing functional groups;
- D) one or more negative tone imaging polymeric resins containing functional groups

that are reactive with the functional groups in the crosslinking agent; and

- E) the dissolution rate modifier according to claim 1.

24. The composition according to claim 23, wherein the crosslinking agent (C) can be activated by an acid generated by the photoacid generator (B).

25. The composition according to claim 23, wherein the functional group of the crosslinking agents is one or more selected from the group consisting of methylol, alkoxyalkyl and carboxymethyl group substituted phenols; methylol, alkoxyalkyl and carboxymethyl group substituted cyclic ureas; methylol, alkoxyalkyl and carboxymethyl group substituted melamines; and methylol, alkoxyalkyl and carboxymethyl group substituted benzoguanine compounds.

26. The composition according to claim 23, wherein the photoacid generator (B) is one or more selected from the group consisting of triflates, pyrogallols, onium salts, hexafluoroarsenates, trifluoromethanesulfonates, esters of hydroxyimides,  $\alpha,\alpha'$ -bis-sulfonyl-diazomethanes, sulfonate esters of nitro-substituted benzyl alcohols and naphthoquinone-4-diazides.

27. The composition according to claim 23, wherein the solvent (A) is one or more selected from the group consisting of propylene glycol methyl ether acetate, cyclohexanone, butyrolactate, and ethyl lactate.

28. The composition according to claim 23, wherein the negative tone imaging polymers contain one or more functional groups selected from the group consisting of hydroxyl, carboxyl, and epoxy.

29. The composition according to claim 23, wherein the negative tone imaging polymers comprise polymers having repeat units derived from polycyclic olefin monomers.

30. A positive tone photoresist composition comprising:

- A) a solvent;
- B) a photosensitive acid generator;
- C) one or more positive tone imaging polymers including a functional group containing moiety that contains a group that can be cleaved when exposed to radiation, rendering the polymer more soluble to a developer than the unexposed polymer, and
- D) the dissolution rate modifier according to claim 1.

31. The positive tone photoresist composition according to claim 30, wherein the positive tone imaging polymer is selected from the group consisting of polynorbornenes, phenolic binders, polyhydroxystyrene, styrene-acrylate copolymers, homopolymers and copolymers of (meth)acrylate esters of alkyl alcohols having from 1 to about 12 carbon atoms, copolymer of norbornene and maleic anhydride, terpolymers of norbornene, maleic anhydride, and combinations thereof.

32. The positive tone photoresist composition according to claim 30, wherein the solvent is a spinning solvent selected from propylene glycol methyl ether acetate, ethyl lactate, cyclohexanone, and combinations thereof.

33. The positive tone photoresist composition according to claim 30, further comprising a base quencher selected from tetramethylammonium hydroxide, triethanolamine, triisopropylamine, N-methylpyrrolidone, and the like.

34. A method of generating a negative tone resist image comprising:

- (a) coating a substrate with a film containing the negative tone photoresist composition according to claim 23 to form a film;
- (b) imagewise exposing the film to radiation to form an image;

29. The composition according to claim 23, wherein the negative tone imaging polymers comprise polymers having repeat units derived from polycyclic olefin monomers.

30. A positive tone photoresist composition comprising:

- A) a solvent;
- B) a photosensitive acid generator;
- C) one or more positive tone imaging polymers including a functional group containing moiety that contains a group that can be cleaved when exposed to radiation, rendering the polymer more soluble to a developer than the unexposed polymer, and
- D) the dissolution rate modifier according to claim 1.

31. The positive tone photoresist composition according to claim 30, wherein the positive tone imaging polymer is selected from the group consisting of polynorbornenes, phenolic binders, polyhydroxystyrene, styrene-acrylate copolymers, homopolymers and copolymers of (meth)acrylate esters of alkyl alcohols having from 1 to about 12 carbon atoms, copolymer of norbornene and maleic anhydride, terpolymers of norbornene, maleic anhydride and combinations thereof.

32. The positive tone photoresist composition according to claim 30, wherein the solvent is a spinning solvent selected from propylene glycol methyl ether acetate, ethyl lactate, cyclohexanone, and combinations thereof.

33. The positive tone photoresist composition according to claim 30, further comprising a base quencher selected from tetramethylammonium hydroxide, triethanolamine, triisopropylamine, N-methylpyrrolidone and the like.

34. A method of generating a negative tone resist image comprising:

- (a) coating a substrate with a film containing the negative tone photoresist composition according to claim 23 to form a film;
- (b) imagewise exposing the film to radiation to form an image;

- (c) post exposure baking the film; and
- (c) developing the image.

35. The method of claim 34, wherein the substrate comprises one or more of silicon, ceramics or polymers.

36. The method of claim 34, wherein the film is coated on the substrate using one or more methods selected from spin coating, spray coating and doctor blading.

37. The method of claim 34, wherein before the film is exposed to radiation in (b), the film is heated to from 90°C to 150°C for from 30 seconds to 5 minutes.

38. The method of claim 34, wherein the film can be imagewise exposed from a radiation source selected from mercury lamps, mercury/xenon lamps, xenon lamps, argon fluoride lasers, krypton fluoride lasers, fluorine lasers, x-rays and electron beams.

39. An integrated circuit assembly method comprising:

- (a) coating a substrate with the negative tone photoresist composition according to claim 23;
- (b) imagewise exposing the film to radiation;
- (c) post exposure baking the film;
- (d) developing the image to expose the substrate; and
- (e) forming the circuit in the developed film on the substrate.

40. An integrated circuit chip, multichip module, or circuit board including the integrated circuit provides by the method of claim 39.

41. A method of generating a positive tone resist image comprising:

- (a) coating a substrate with a film containing the positive tone photoresist composition according to claim 30 to form a film;
- (b) imagewise exposing the film to radiation to form an image;

- (c) post exposure baking the film; and
- (d) developing the image.

42. An integrated circuit assembly method comprising:

(a) coating a substrate with the positive tone photoresist composition according to claim 30;

- (b) imagewise exposing the film to radiation;
- (c) post exposure baking the film;
- (d) developing the image to expose the substrate; and
- (e) forming the circuit in the developed film on the substrate.

43. An integrated circuit chip, multichip module, or circuit board including the integrated circuit provides by the method of claim 42.